**Precipitation and characterization of vanadium V(II), V(III) and V(V) sulfate compounds in Vanadium Redox Flow Battery electrolyte**

Waldemir M. Carvalho Jr.\*, Laurent Cassayre, Theodore Tzedakis, Fabien Chauvet, Ranine El-Hage, Béatrice Biscans.

*Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France*

*\*Corresponding author: waldemir.mouradecarvalho@ensiacet.fr*

**Highlights**

* V(II), V(III) and V(V) supersaturated solutions were prepared by electrolytic dissolutions of commercial vanadium salt in sulphuric acid solutions.
* Pure crystals of hydrated V(II), V(III) and V(V) sulfates (VSO4·7H2O, V2(SO4)3·10H2O and V2O5·1.5H2O) were isolated and identified as precipitating phases, in different conditions.

**1. Introduction**

The vanadium redox flow battery (VRFB) has been receiving considerable attention in recent years, as one of the most viable energy storage technologies for large-scale application. It eliminates the cross-contamination present in flow battery, enables long cycle life (>10000 cycles), high-energy efficiencies and relatively low-cost structure for large storage capacities [1]. As the concentration of vanadium species in the H2O-H2SO4 electrolyte determines the VRFB energy density, high concentrations are required. Meanwhile, major precipitation of vanadium compounds must be avoided [2]. Despite current researches aiming at understanding the vanadium salts precipitation in a VRFB, very little has been done to identify the phases precipitated in the vanadium acidic solution used as VRFB electrolyte. This study has thus focused on (i) preparing V(II), V(III) and V(V) supersaturated solutions (ii) identifying the precipitation products in VRFB operating conditions, with an aim of improving the understanding of vanadate chemistry in a high concentrated sulphuric acid solution.

**2. Methods**

The vanadium supersaturated solutions are prepared by dissolution of commercial VOSO4 powder suspension, and subsequent electrochemical oxidation (for V(V) preparation) or reduction (for V(II) and V(III) preparation) in one of the compartment of a two-compartment electrolytic cell separated by a Nafion cationic membrane. Thick carbon felts (5mm) were used as anode and cathode. Based on the solubility curves of the vanadium salts available in the literature [2], 60.63 grams of VOSO4 powder (corresponding to 5 mol L-1) were added in 50 mL of a 5 mol L-1 H2SO4 solution, and placed either into the negative half-cell to prepare V(II) and V(III) supersaturated sulfate solution, or into the positive half-cell to prepare V(V) sulfate solution. The galvanostatic electrolyzes were run at a constant current density (1 A) with a DC power supply. The vanadium species concentration was followed by UV-vis spectroscopy for V(II) and V(III) solution and by titration for V(V) solution. When the required vanadium conversion was achieved , the supersaturated solution was transferred to another vessel where they were aged at constant temperature (30 °C for V(II) or V(III) and 60 °C for V(V)) and at constant agitation (400 rpm), while the vanadium species concentrations were monitored until precipitation occurred. The precipitated products were then filtrated, washed with ethanol, dried at 60 °C for 4 hours, and analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and UV-Vis spectroscopy.

**3. Results and discussion**

The initial vanadium concentrations were measured before the aging process as 3.2, 3.5 and 4.0 mol L-1 for V(II), V(III) and V(V) solutions, respectively. Significant amounts of precipitated solids were obtained in V(II) and V(III) solutions, after 12 h (purple precipitate for V(II) and green precipitate for V(III)). For the V(V) solution, 11 days were required to produce enough solid (orange/brown precipitate) for further characterization. The obtained precipitated powders were then diluted in a sulphuric acid solution and analyzed by UV-Vis spectroscopy. They all showed their own specific absorption profile, confirming that each of the precipitates corresponds to a specific oxidation state, depending on the initial solution. Powder XRD analysis of each of the dried precipitates was performed (Figure 1). The precipitate obtained from the V(II) solution perfectly match the VSO4·7H2O phase, and the solid produced from V(III) and V(V) solutions fairly match V2(SO4)3·10H2O and V2O5·1.5H2O phases, respectively. These phases were similar for different aging/precipitation durations. To confirm the V(III) and V(V) precipitates identification, the powders were heat-treated at 200 °C in air and analyzed again by XRD. This temperature (200 °C) was determined by TGA. It enables a complete removal of the water from the hydrates without any decomposition (to SO3 for example) nor any phase transition (due to oxidation for instance). After the heat treatment, the V(III) and V(V) precipitates perfectly match the V2(SO4)3 and V2O5 pattern respectively.



**Figure 1.** X-ray diffraction pattern of the precipitation product of the (a) V(II), (b) V(III) and (c) V(V) solution after aging.

**4. Conclusions**

In summary, we report a method to prepare V(II), V(III) and V(V) supersaturated solutions in an H2SO4-H2O electrolyte, from the only vanadium sulfate compound commercially available (VOSO4). We also identify the precipitation products which may form in a VRFB operated with such supersaturated solutions. The results showed that V(II), V(III) and V(V) sulfate solutions precipitate as VSO4, V2(SO4)3 and V2O5 hydrates and not in their anhydrous form. Taking into account this hydration degree might change the vanadium concentration limits of a VRFB and the occurrence of precipitation which are currently calculated in the literature with the anhydrous form [1].

**References**

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